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(54) TOOL MATERIAL FOR FIRING CERAMIC HAVING COATED LAYER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a tool material for firing ceramics having a zirconia coated layer which reacts less with ceramic products, is hardly peelable in spite of repetitive use and is highly durable.

SOLUTION: The zirconia coated layer of  $\geq 15$  to  $\leq 44$   $\mu\text{m}$  in the arithmetic mean roughness (Ra) of the coating surface and  $\geq 50$  to  $\leq 69\%$  in the void volume over the entire part of the coated layer is formed by spraying a zirconia coating material to the surface of the base material of the tool material for firing the ceramics, then firing the same. Accordingly, the reaction with the ceramic products to be fired is lessened, the peeling resistance in repetitive use is improved and the durability of the tool material for firing may be improved.

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CLAIMS

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[Claim(s)]

[Claim 1] Instrument material for ceramic baking to which arithmetic mean granularity (Ra) of this coating is characterized by 15-micrometer or more being 44 micrometers or less in the instrument material for ceramic baking which calcinates and changes after spraying a zirconia coating material on a base material front face.

[Claim 2] Instrument material for ceramic baking to which voidage of this coating layer is characterized by 50% or more being 69% or less in the instrument material for ceramic baking which calcinates and changes after spraying a zirconia coating material on a base material front face.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to instrument material for ceramic baking, such as the sagger and shelf board which are used in order to calcinate ceramic components for electronic industry, such as a ceramic product especially a ceramic condenser, and a ferrite, and a setter.

[0002]

[Description of the Prior Art] When calcinating ceramic products for which need is increasing rapidly by the spread of a cellular phone, personal computers, etc., such as a ceramic condenser and a ferrite, arranging a Plastic solid in on the instrument material for baking which performed zirconia coating with few reactions with this ceramic product, and calcinating at 1200-1400 degrees C is performed. Being heated by homogeneity is important while a controlled atmosphere touches this ceramic product at homogeneity in that case.

[0003] After making the thing and zirconia which depend a zirconia on the approach of carrying out thermal spraying on a base material as instrument material for baking which performed the above-mentioned zirconia coating adhere on a base material, there are some which are depended on the approach of calcinating. What depends a zirconia on the approach of carrying out thermal spraying is excellent in reactivity-proof in order to carry out thermal spraying of the electromelting zirconia powder, and since the arithmetic mean granularity on the front face of coating (Ra) has adhered to the base material powerfully satisfactory on a reaction in about 15 micrometers, voidage cannot exfoliate easily at least about 20%, and is used widely. The arithmetic mean granularity on the front face of coating of the instrument material for baking which formed the coating layer by calcinating on the other hand after making a zirconia coating material adhere (Ra) is less than 10 micrometers, and the many are 5-6 micrometers. There is a thing of the grain-size configuration which combined the thing and the aggregate which consisted of only fines, and fines as structure of the zirconia coating layer by baking of these former, and the voidage is about 30%. Especially voidage is made about 35% high, the stress by the expansion contraction accompanying heating cooling is eased, and there are some which raised peeling resistance.

[0004]

[Problem(s) to be Solved by the Invention] Although the approach of forming a zirconia coating layer by baking is desirable since cost is low compared with thermal spraying, there is a problem that reactivity-proof and endurance equivalent to what is depended on thermal spraying are not acquired. After making a zirconia adhere, by the instrument material for baking which calcinated and formed the coating layer, if the arithmetic mean granularity on the front face of coating (Ra) is small, since there is much contact surface with this ceramic product, it will be easy to produce a reaction, and when voidage is low, there is a problem of being easy to exfoliate since adhesion force with a base material is also weak. In order to raise voidage, making voidage high combining the coarse grain of the low electromelting zirconia of a degree of sintering and the superfines of a electromelting zirconia is performed in the zirconia coating layer, but since the degree of sintering is low, the reinforcement of a coating layer produces

BOROTSUKI small. In order to raise the reinforcement of a coating layer, when a coating layer with low voidage is made only using the superfines of a zirconia, exfoliation is produced according to the difference of coefficient of thermal expansion with a base material, and there is a problem from which sufficient durability is not obtained.

[0005] If a use count is piled up and this ceramic product component permeates also in the zirconia coating layer by thermal spraying it is supposed on the other hand that it excelled in reactivity-proof and endurance compared with the zirconia coating layer by the conventional baking, a reaction progresses, it exfoliates and the base material serves as the cast away in the usable condition. Since a particle becomes [ the particle which fused the zirconia by the approach of carrying out thermal spraying ] flat in a base material at high speed, it is difficult to set arithmetic mean granularity on the front face of coating (Ra) to 15 micrometers or more. The above-mentioned trouble is solved, also when a reaction with this ceramic product is reduced and used repeatedly, it is hard to generate exfoliation of a coating layer, and this invention aims at offering the instrument material for ceramic baking excellent in endurance.

[0006]

[Means for Solving the Problem] In the instrument material used in order that this invention may calcinate a ceramic product, in order to attain the above-mentioned purpose, after spraying a zirconia coating material on the base material front face of this instrument material for baking, by calcinating, the arithmetic mean granularity on the front face of coating (Ra) is 15 micrometers or more 44 micrometers or less, and makes it a summary for voidage to form the zirconia coating layer which is 69% or less 50% or more.

[0007]

[Function] In this invention, after spraying a zirconia coating material on a base material, the arithmetic mean granularity on the front face of coating (Ra) is 15 micrometers or more 44 micrometers or less in calcinating, and when voidage forms 69% or less of zirconia coating layer 50% or more, reactivity-proof with this ceramic product and peeling resistance can be raised. Since there was much contact surface with a ceramic product, while the arithmetic mean granularity (Ra) of a zirconia coating layer became easy to react in less than 15 micrometers, since voidage's becoming less than 50% and it being easy to produce heating and exfoliation by repetition of cooling and arithmetic mean granularity (Ra) became [ voidage ] as high as 70% or more in 45 micrometers or more and the bonding strength of a zirconia particle became weak, BOROTSUKI was produced, and it found out that endurance was inferior as a result of the experiment.

[0008] Next, the instrument material for baking of this invention is explained to a detail. The instrument material for baking which it was desirable to include the superfines high grade zirconia powder by the wet method excellent in the degree of sintering in a zirconia coating layer, could be made to sinter a zirconia particle firmly, did not produce BOROTSUKI even if voidage was large, and was excellent in endurance is obtained. A zirconia coating layer is constituted by a electromelting zirconia and the superfines high grade zirconia, and in order to acquire sufficient bonding strength, 5% of the weight or more of the whole coating layer of the content of a superfines high grade zirconia is desirable [ a layer ]. As a superfines high grade zirconia, there are stabilization, non-fully stabilized zirconia, etc. whose specific surface area obtained by carrying out temporary quenching of the zirconium compound obtained by wet processes, such as a coprecipitation method and the hydrolyzing method, at 400-1000 degrees C is 5-20m<sup>2</sup>/g, and it fully sinters by calcinating at 1400 degrees C for 3 hours or more. Therefore, by calcinating a zirconia above 1400 degrees C after spraying and desiccation to a base material, a zirconia particle is firmly burned on a base material, and the zirconia coating layer which BOROTSUKI cannot produce easily is obtained.

[0009] Next, the manufacture approach of the instrument material for ceramic baking of this invention is explained. First, as a base material of the instrument material for baking of this invention, the quality of the materials usually used for the instrument material for ceramic baking, such as quality of an alumina, quality of an alumina-silica, quality of a silicon carbide-silica, and quality of silicon carbide-silicon nitride, can be used. As the manufacture approach of a base material, raw material powder is fabricated by the press or cast after mixing and kneading, and is calcinated after desiccation. Especially the base

material after baking does not perform surface treatment, such as blasting. Therefore, although the arithmetic mean granularity on the front face of a base material (Ra) changes with grain-size configurations of a base material etc., the arithmetic mean granularity on the front face of a base material of the instrument material for ceramic baking for electronic industry (Ra) is less than 10 micrometers, and the many are usually 5-6 micrometers. Next, the manufacture approach of the coating layer concerning this invention is explained. After mixing and slurring a electromelting zirconia, a superfines high grade zirconia, and a liquid binder, a coating material is sprayed on a base material front face with a spray gun at granularity, and a coating layer is formed, making granulation deposit. In that case, by changing the distance of a base material and a spray gun, the arithmetic mean granularity on the front face of coating (Ra) can be adjusted, and the voidage of a coating layer can also be adjusted to coincidence. That is, the voidage inside a coating layer becomes high, so that the distance of a base material and a spray gun is far, surface arithmetic mean granularity (Ra) becomes large, voidage becomes low and arithmetic mean granularity (Ra) becomes small, so that it is near. Therefore, if the distance is too near, to a base material, a coating material will not adhere, will slur at granularity, a coating front face will become smooth, and voidage will become low. However, since the distance of a base material and a spray gun changes with the conditions besides absorptivity of the diameter of a nozzle, or a base material, spraying distance is determined, taking those conditions into consideration. Even if thermal shock resistance improves and uses it repeatedly by being able to enlarge arithmetic mean granularity (Ra) of a zirconia coating layer, being hard coming to react since the contact surface with this ceramic product decreases, and making voidage high at coincidence, if it calcinates after spraying a coating material on a base material at granularity, it is hard to generate exfoliation of a zirconia coating layer, and the instrument material for ceramic baking excellent in endurance can be obtained.

[0010]

[Example] The example of this invention is shown below and the place by which it is characterized [ of this invention ] is clarified further.

[0011] (Examples 1-4) It mixed and kneaded by the approach same with manufacturing the usual refractories, it calcinated at 1700 degrees C for 5 hours after fabricating in configuration of 150x150x5mm, and the nature (20390 % of the weight [ of aluminum ], 210 % of the weight of SiO(s)) base material of an alumina-silica whose arithmetic mean granularity (Ra) is 5 micrometers was manufactured. Next, it mixed at a rate of 70 % of the weight (292 % of the weight [ of ZrO(s) ] Y 2O38 % of the weight) of electromelting yttria-stabilized-zirconia powder with a particle size of 5-15 micrometers, and 30 % of the weight of high grade yttria-stabilized-zirconia powder by the coprecipitation method with a particle size of 0.1-1 micrometer (295 % of the weight [ of ZrO(s) ] Y 2O35 % of the weight), and to this, the PVA water solution was added 5%, and it slurred, and considered as the coating material. This coating material was sprayed from a different distance on the above-mentioned base material, and the zirconia layer whose surface arithmetic mean granularity (Ra) is 15 micrometers, 20 micrometers, 30 micrometers, and 44 micrometers was formed. And calcinated at 1500 degrees C after desiccation for 5 hours, the zirconia coating layer with a thickness of 0.2mm was made to form, and the instrument material for ceramic baking was produced. In order to investigate such peeling resistance, the Plastic solid of barium titanate was laid on zirconia coating, and the condition of a repetition coating layer was investigated for forced-air cooling to a room temperature 200 times after heating at 1300 degrees C. The result of having investigated the peeling resistance about the above-mentioned examples 1-4 is shown in Table 1. In addition, voidage measured the thickness of a coating layer, from the zirconia weight and adhesion area of an adhering coating layer, asked for the bulk density of a zirconia coating layer, and asked for it by \*(ing) bulk density for which it asked by the specific gravity 6 of a zirconia. Moreover, the arithmetic mean granularity (Ra) of a coating layer is JIS. B It measured according to 0601-1994.

[0012] (Examples 1-4 of a comparison) The arithmetic mean granularity on the front face of coating (Ra) made the zirconia coating layer whose voidage is 30%, 49%, 70%, and 73%, respectively form by 5 micrometers, 14 micrometers, 45 micrometers, and 53 micrometers by the same approach as examples

1-4 for a comparison, and this was made into the examples 1-4 of a comparison. In addition, the result of having investigated the peeling resistance about the examples 1-4 of a comparison is shown in Table 1.

[0013]

[Table 1]

	噴霧距離 (cm)	算術平均粗 さ Ra ( $\mu$ m)	空隙率 (%)	1300℃の繰返 しにより剥離 が発生した回 数	1300℃繰返し 試験 200 回後 の表面状態
実施例 1	8 0	4 4	6 9	2 0 0 回以上	剥離なし
実施例 2	5 5	3 0	6 5	2 0 0 回以上	剥離なし
実施例 3	4 0	2 0	6 0	1 5 2 回	部分剥離
実施例 4	3 0	1 5	5 0	6 6 回	部分剥離
比較例 1	2 0	5	3 0	1 5 回	半分剥離 亀甲状クラック
比較例 2	2 8	1 4	4 9	3 4 回	部分剥離 亀甲状クラック
比較例 3	8 2	4 5	7 0	2 0 0 回以上	剥離なし ボロツキ小
比較例 4	9 0	5 3	7 3	2 0 0 回以上	剥離なし ボロツキ大

[0014] If spraying conditions are changed, it sprays on a base material and it calcinates after desiccation as shown in Table 1 The arithmetic mean granularity (Ra) of a zirconia coating front face 15 micrometers, 20 micrometers, Are 30 micrometers and 44 micrometers and voidage in the examples 1-4 which were 50%, 60%, 65%, and 69%, respectively Voidage by 5 micrometers and 14 micrometers, respectively 30%, [ arithmetic mean granularity (Ra) ] Compared with 49% of example 1 of a comparison, and the example 2 of a comparison, are hard to produce a reaction, and the peeling resistance by the heat cycle is improving. Moreover, it turns out that there is no BOROTSUKI [ like / in 45 micrometers and 53 micrometers / voidage / the example 3 of a comparison which are 70% and 73%, respectively, and the example 4 of a comparison ] whose arithmetic mean granularity (Ra) is, and it excels in endurance.

[0015] (Example 5) The silicon carbide raw material whose SiC purity is 99% or more was blended, press forming was carried out to the configuration of 250x250x5mm after a binder, mixing, and kneading, it calcinated at 1400 degrees C after desiccation and among atmospheric air for 5 hours, and the nature (92-% of the weight [ of SiC(s) ], 28 % of the weight of SiO(s)) base material of a silicon carbide-silica whose arithmetic mean granularity (Ra) is 7 micrometers was produced. Next, it was made to dry after spraying on the above-mentioned base material after adding a binder to alumina powder, mixing and considering as a slurry, and forming an alumina layer with a thickness of 0.1mm. Furthermore, it blended at a rate of 90 % of the weight (296 % of the weight of ZrO(s), 4 % of the weight of CaO(s)) of calcia fully stabilized zirconia of electromelting, and 10 % of the weight of high grade yttria stabilized zirconia with a particle size of 0.1-1.0 micrometers (287 % of the weight [ of ZrO (s) ] Y 2O3 8 % of the weight), the PVA water solution was added to this 5%, and it mixed for 8 hours, and considered as the coating material. After it sprayed this zirconia coating material on the above-mentioned alumina coating layer and the arithmetic mean granularity on the front face of coating (Ra) made the zirconia coating layer with a thickness of 0.3mm whose voidage is 60% in 20 micrometers form, it calcinated at 1400 degrees C for 5 hours, and the instrument material for baking was produced. Although the base of a ferrite core was laid on this zirconia coating and baking at 1350 degrees C was repeated 100 times, exfoliation of a coating layer was not seen, and the abnormality grain growth in the contact surface with the zirconia coating layer of a ferrite core was not seen, but showed good reactivity-

proof.

[0016] In addition, this invention is not limited to the above-mentioned example, and can be applied within the limits of the summary of this invention about a class, a rate of stabilization, etc. of a stabilizing agent (CaO, Y<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> grade) of the quality of the materials (the quality of an alumina, quality of an alumina-silica, quality of a silicon carbide-silica, etc.) of the base material which constitutes the instrument material for baking, and a zirconia coating layer. [ of fully stabilized zirconia ]

[0017]

[Effect of the Invention] Like the above explanation, the instrument material for ceramic baking of this invention It calcinates, after spraying a zirconia coating material on a base material front face. The arithmetic mean granularity on the front face of coating (Ra) by 15 micrometers or more 44 micrometers or less When the voidage of the whole coating layer forms the zirconia coating layer which is 69% or less 50% or more, a reaction with the ceramic product calcinated is reduced, the peeling resistance in repetition use is improved, and the endurance of the instrument material for baking can be raised.

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[Translation done.]